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PETROLOGY OF THE KOKINO VOLCANIC ROCKS, KUMANOVO DISTRICT, REPUBLIC OF MACEDONIA

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Abstract

The Locality Kokino in the Republic of Macedonia is of particular interest as archaeological site (Bronze Age megalithic observatory). It is built of Paleogene volcanic rocks that are the subject of the present petrological study.

For the aims of the study 20 samples have been collected, ten of them being thoroughly examined. All samples have been studied with chemical analyses, microscopic examinations and geochronological analyses, and determined as trachydacites of the shoshonitic series with porphyritic structure and massive texture. The age has been determined by K-Ar method as Early Oligocene (ca. 30 Ma).

Key words: petrology, volcanic rocks, Kokino locality

Introduction. The Bronze-Age archaeological site Kokino is situated in the area of Tatichev Kamen (between 1010 m and 1030 m above sea level) approximately 30 km NE from the town of Kumanovo and about 6 km from the Serbian border, in the Staro Nagorichane municipality. The area of the site is about 90 by 50 m. It was discovered in 2001 by the archaeologist Jovica Stankovski, Director of the National Museum in Kumanovo, and it is one of the rare and protected observatories in the world. It has been nominated as a UNESCO World Heritage site by the Macedonian Ministry of Culture, and for time being is on the tentative list.

For studying the rocks from this locality we collected 20 samples and performed petrological examinations of ten of them. Each of the ten samples has been studied by chemical analysis, rare earth and trace elements analysis, microscopic examination in thin section. Two samples have been studied for $^{87}Sr/^{86}Sr$ isotopic composition, and two phenocryst minerals from one sample have been dated by K/Ar method.

Geological setting. The locality Kokino consists of rocks that belong to the earliest phase of the Tertiary volcanic activity in the Kratovo-Zletovo area. The rocks occur in the form of a volcanic neck [11], and possess a typical vertical columnar jointing. The colour of the rocks is dirty white, gray to gray green, depending on the extent of surface weathering.

The Kratovo-Zletovo volcanic area is the largest magmatic area in Macedonia (surface of about 1200 km^2), and is situated in the eastern part of the country [13]. Different opinions for its regional geotectonic position are published. Some of them place the area in the Serbo-Macedonian massif [10], but according to others it is situated in the Vardar zone, [1, 7]. The Kratovo-Zletovo volcanic area includes the ore region of the same name, thus it is of great interest from magmatic and metallogenic point of view. According to [2, 13] and other researchers the volcanic activity in Kratovo-Zletovo area started at the end of the Eocene or in the Early Oligocene, and with some pauses lasted up to the Early Pliocene. In that period, volcanic activity was successively moved from north-east to south-west [5]. The volcanism in the region was generally controlled by deep sub-meridional dislocations, activated by Paleogene east-west extension. To the end of the Miocene, the volcanic activity was reestablished along longitudinal neotectonic dislocations, starting with younger north-south extension. Geomorphologically, in Kratovo-Zletovo area there are about 20 volcanic centres and calderas, highly eroded by postvolcanic denudation processes.

The volcanic rocks in the Kratovo-Zletovo area belong to a large Eocene-Oligocene magmatic belt which can be traced from Serbia to the west and to Bulgaria and Turkey to the east [9]. The explosive magmatism generated abundant volcanic rocks (lavas and pyroclastics) and subvolcanic bodies of predominantly andesitic, trachyandesitic, dacitic and rhyolitic composition. Numerous investigations show the calc-alkaline to shoshonitic character of the magmatism, and only few of them refer it to the tholeiitic series [13].

Analytical methods. Major and trace elements of 10 samples from locality Kokino have been analysed by OES ICP Method in Sofia and Laser Ablation Inductively Coupled Plasma (LA-ICP-MS) at the Mass Spectrometry Laboratory, Geological Institute – BAS, Sofia, respectively. The samples have been chosen after microscopic examination of the thin sections. Two samples have been analysed for $^{87}Sr/^{86}Sr$ isotopic ratios at the Institute for Geochemistry and Petrology in Zurich, Switzerland (Table 1). Two K/Ar measurements were performed at the Institute for Nuclear Research, Hungarian Academy of Sciences, in Debrecen, Hungary (Table 2).

Age and characteristics of the rocks from Kokino. K/Ar age determination yielded 30.6±2.1 Ma on the K - feldspar and 31.3±1.3 Ma on the biotite, demonstrating that the magmatic activity in Kokino is of Early Oligocene age (Table 2).

The microscopic studies of all 10 thin sections show identical mineral com-

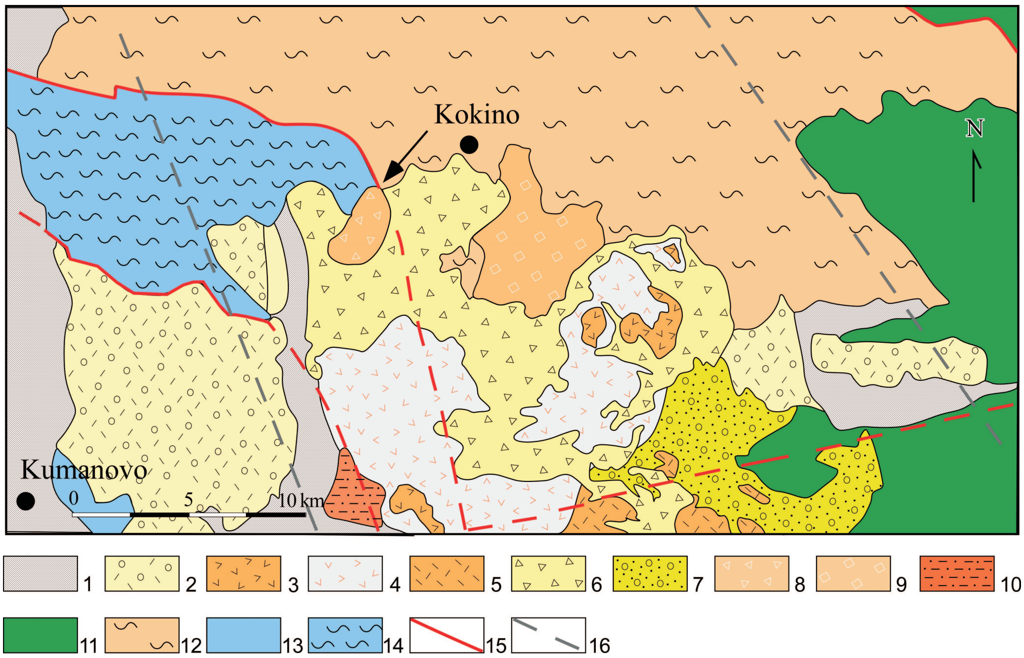

Fig. 1. Geological map of the Locality Kokino. After (Grozdev, 2014). Legend: 1. Quaternary: Alluvial deposits (gravels, sands, clays); 2–4: Neogene: 2 – Undivided gravels, sands and clays (200–500 m); 3 – Lava flows and centres (latites); 4 – Pyroclastics (latitic-ignimbrites, 0–200 m); 5–10: Paleogene: 5 – Lava flows and centres (latites); 6 – Lava breccias (volcanic breccia: 200–550 m); 7 – Stone dolls (volcanoclastic sediments: 100–300 m); 8 – Hydrothermally altered volcanics (andesites, dacites); 9 – Lava flows and centres (trachytes and trachydacites); 10 – Flysch (sandstones, siltstones, conglomerates, tuffs 500–750 m); 11–14: Pre-Paleogene complexes and units: 11 – Morava unit = upper complex; 12 – Lower complex/Ograzden unit; 13 – Vardar zone, Central subarea; 14 – Vardar Zone, East subarea; 15. Faults; 16. Boundaries of the magmatic zone

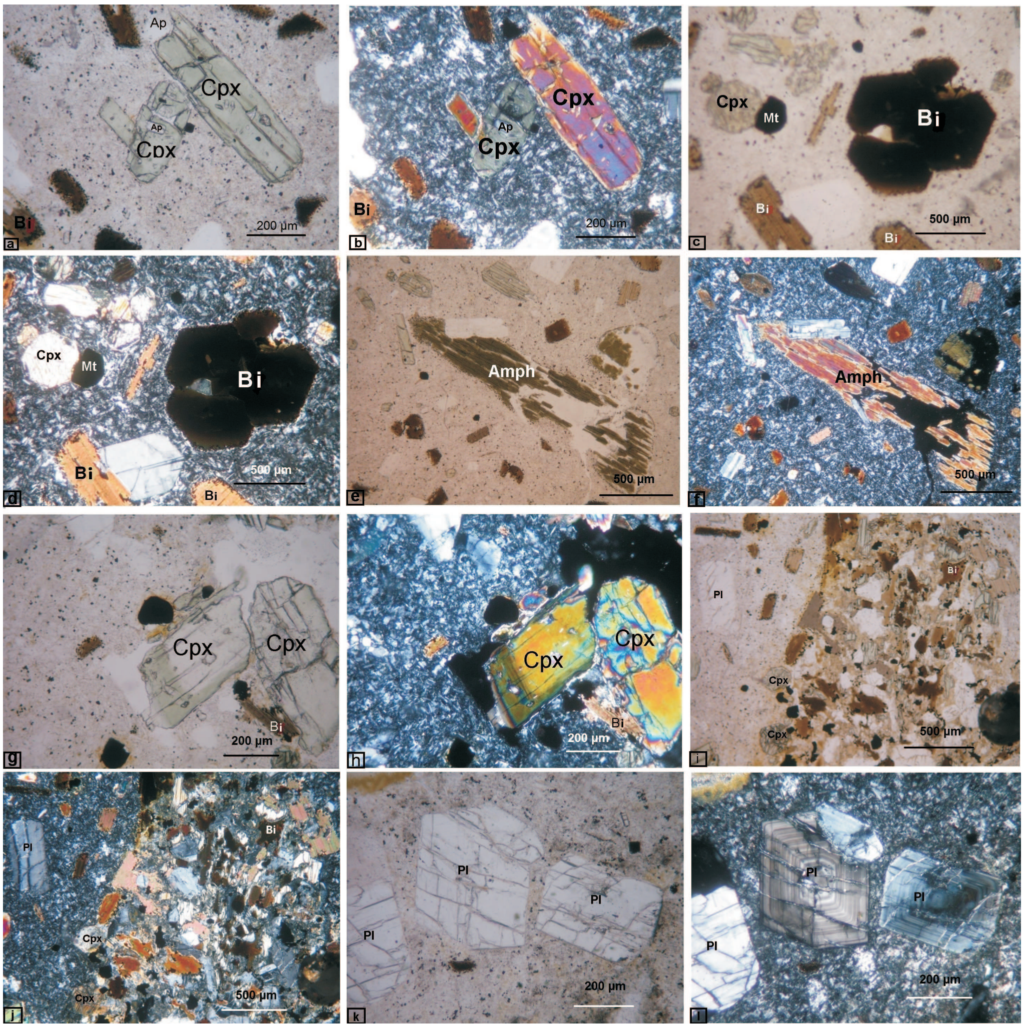

Fig. 2. Photomicrographs of thin sections from Kokino volcanics. Photomicrographs of sample No 1. (a–f) Microlithic groundmass. Structure: porphyritic, texture: massive. Cpx – clinopyroxene, Ap – apatite, Bi – biotite, Mt – magnetite, Amph – amphibole: (a) clinopyroxene – (green) with fine crystals of apatite – (white). //P (X10); (b) clinopyroxene – (green) with fine crystals of apatite – (white).+P (X10); (c) biotite (with fine crystals of magnetite at the periphery), magnetite and clinopyroxene. //P (X5); (d) biotite, magnetite and clinopyroxene. +P (X5); (e) big crushed crystal of amphibole. //P (X10); (f) big crushed crystal of amphibole. +P (X10); Photomicrographs of sample No 3. (g, h) Microlithic groundmass. Structure: porphyritic, texture: massive. Cpx – zonal clinopyroxene, Bi – biotite: (g) zonal clinopyroxene – (the large grains) and biotite. //P (X10); (h) zonal clinopyroxene (the large grains) and biotite +P (X10); Photomicrographs of sample No 4. (i, j) Microlithic groundmass. Structure: porphyritic, texture: massive. Bi – biotite, Cpx – clinopyroxene, Pl – plagioclase: (i) biotite, clinopyroxene and plagioclase. //P (X10); (j) biotite, clinopyroxene and plagioclase. +P(X10); Photomicrographs of sample No 12. (k, l) Microlithic groundmass. Structure: porphyritic, texture: massive. Pl – plagioclase: (k) oscillating zonal plagioclase //P (X10); (l) oscillating zonal plagioclase +P (X10)

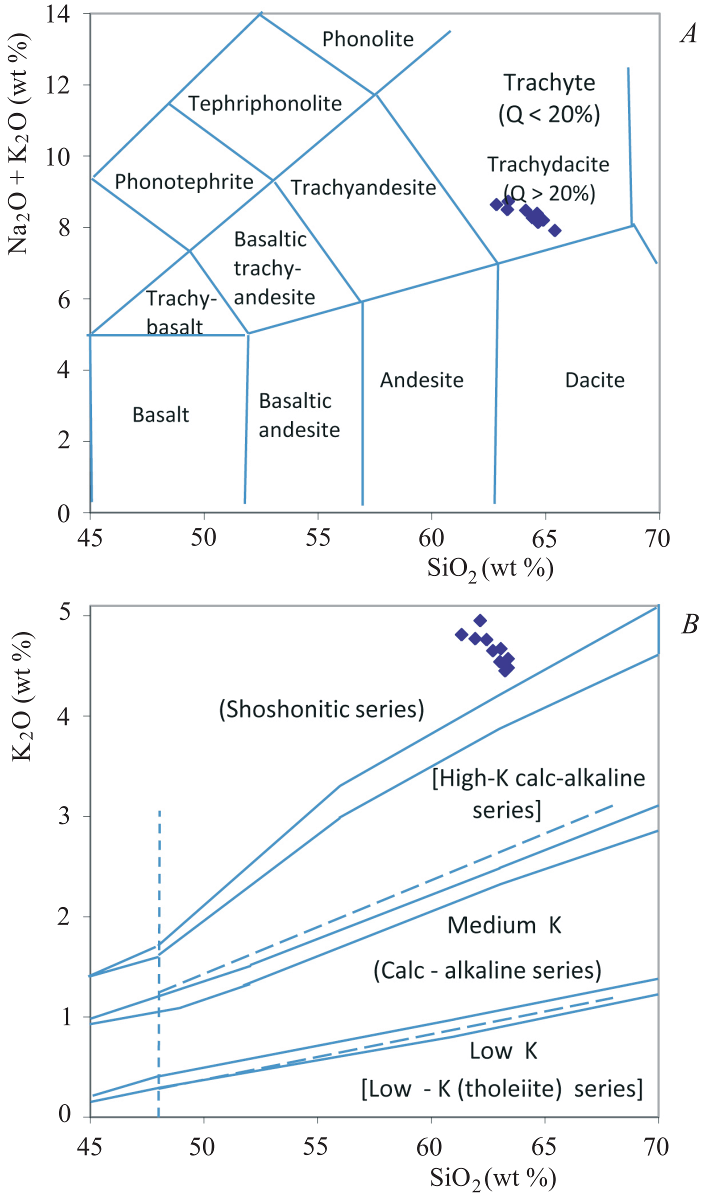

Fig. 3. *A*) TAS ($Na_2O + K_2O$ vs SiO_2) classification diagram of the Kokino volcanic rocks (Le Bas et al., 1986). *B*) K_2O vs SiO_2 diagram (Peccerilo and Taylor, 1976); series boundary lines after different authors of [12]

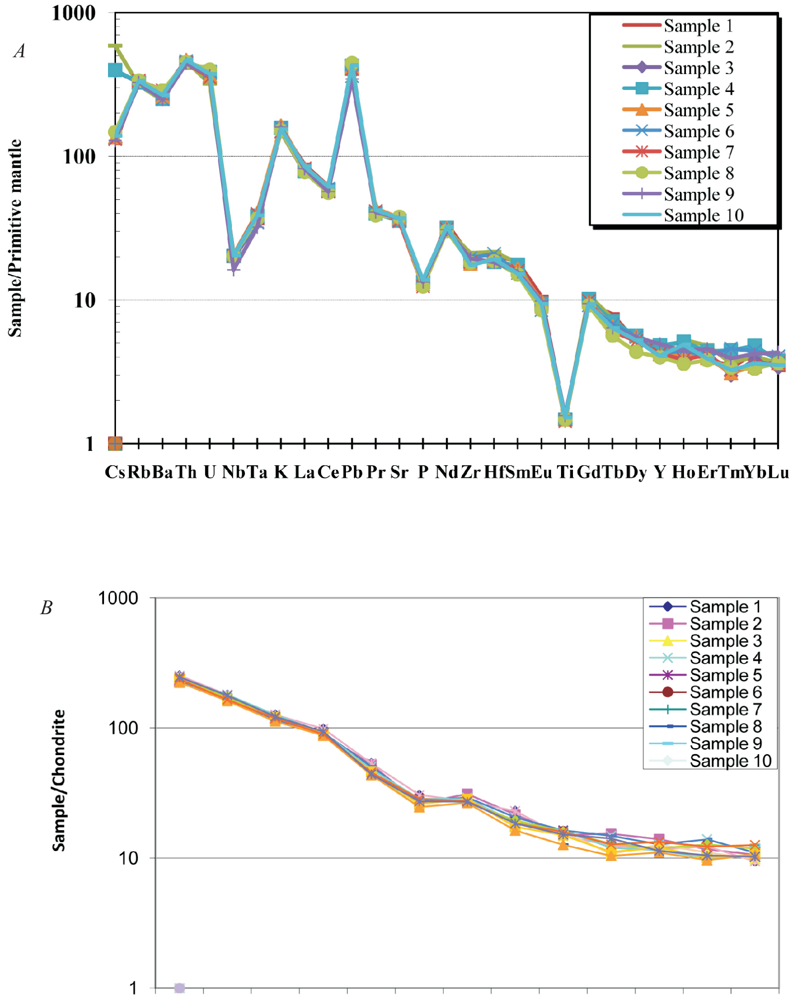

Fig. 4. Trace elements distribution spidergrams: primitive mantle normalized patterns (top) and REE distribution patterns normalized to C1 chondrite values (bottom)

Table 1

Sr and Nd isotope data for samples 1 and 16 from Kokino. $^{87}Rb/^{86}Sr$ and $^{147}Sm/^{144}Nd$ ratios are calculated using the Rb and Sr content from the LA-ICP-MS analyses and the distribution of the isotopes ^{87}Rb, ^{86}Sr, ^{147}Sm and ^{144}Nd

Sample No	Rb, ppm	Sr, ppm	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$	2σ error	$(^{87}Sr/^{86}Sr)_i$ at 30 Ma	Sm, ppm	Nd, ppm	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$	2σ error	$(^{143}Nd/^{144}Nd)_i$ at 30 Ma
1	214	798	0.7585	0.710244	0.000027	0.709921						
16	210	776	0.7623	0.710374	0.000008	0.710049	7.30	42.1	0.1093	0.512212	0.000011	0.512191

position. The rocks are composed of phenocrysts of zonal plagioclase, clinopyroxene, amphibole, biotite, and single sanidine crystals (Fig. 2). Some biotites and amphiboles show opacitic rims. Accessory minerals are apatite and titanium magnetite. Some mafic minerals are partly replaced by chlorite. The groundmass is microlithic, composed mostly of plagioclase and clinopyroxene set in glassy or quartz-feldspar mesostasis.

The results from the major element chemical analyses are shown in Fig. 3. According to the TAS (Na_2O+K_2O vs SiO_2) classification diagram (Le Bas et al., 1986), (Fig. 3*A*), all analysed rocks, after recalculation of major oxides to 100% on a volatile-free basis, fall in the field of trachydacites. Their plots on the K_2O vs SiO_2 diagram of Peccerilo and Taylor, (1976), (Fig. 3*B*) show that the rocks belong to the shoshonitic series.

The Primitive-mantle normalized trace element patterns of the rocks from Kokino (Fig. 4*A*) show high enrichment in LILE (e.g.) and a progressive decrease from HFS to Fe-Mg elements with minima on Ti and Nb contents, typical for the subduction-related magmas.

The REE patterns (Fig. 4*B*) gradually decrease from light REE (LREE) towards heavy REE (HREE) with small negative Eu anomaly.

The measured and age-corrected Sr/Nd isotopic compositions for the 2 studied samples are listed in Table 1. Initial Sr isotopic ratios range between 0.709921 and 0.710049. The values point that the melts were with a significant admixture of crustal material.

Table 2

K/Ar analysis, of two mineral fractions from sample No 1

Mineral	K %	40 Ar (rad) ccSTP/g	40 Ar (rad) %	Age $\pm\sigma$ Ma
Feldspar, $d < 2.64$ g/cm^2	1.412	1.412×10^{-6}	22.3	30.6 ± 2.1
Biotite	7.024	8.617×10^{-6}	58.2	31.3 ± 1.3

Discussion and conclusions. The volcanic rocks from the locality Kokino in Macedonia have been formed at about 31 Ma, during the earliest phase of volcanic activity of the Kratovo-Zletovo area. The rocks form a hill which represents a volcanic neck [11]. The microscopic examinations and the major elements analyses, determine the rocks as potassic trachydacites. The distribution of the Primitive-mantle normalized trace elements (Fig. 4*A*) shows typical subduction-related signature. The small negative Eu anomaly suggests some plagioclase fractionation. The $^{87}Sr/^{86}Sr$ isotopic analyses indicate either large participation of crustal material in their genesis or melting of metasomatised mantle.

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REFERENCES

[1] Arsovski M., R. Petkovski. Geologica Macedonica, **49**, 1975.
[2] Arsovski M. Tectonic of Macedonia, Faculty of Mining and Geology – Shtip, 1997, 306 pp.
[3] Banushev B. Practical Petrography. University "St. Ivan Rilski" – Sofia, Bulgaria, 2006, 324 pp.
[4] Boev B., S. Lepitkova. Geologica Macedonica, **5**, 1990-1991, No 1, 15–30.
[5] Boev B., Y. Yanev. Acta Volcanologica, **13**, 2001, Nos 1–2, 57–71.
[6] Cenev G. Publications of the Astronomical Observatory of Belgrade, No 80, 2006, 313–317.
[7] Dimitrievic M. Geologica Macedonica, 1974, 119–153.
[8] Grozdev V. Unpublished PhD Thesis. Bulgarian Academy of Sciences, 2014, 238 pp.
[9] Harkovska A., Y. Yanev, P. Marchev. Geologica Balcanica , **19**, 1989, No I, 37–72.
[10] Ivanov T. Metallogeny of the Vardar zone. Report, VI Geological Symposium – Ohrid, 1966.
[11] Milevski I. Scientific Annals, Aristotle University of Thessaloniki, **99**, 2010, 475-482.
[12] Rollinson R. H. Using of Geochemical Data. Pearson Education Limited – England, 1993, 380 pp.
[13] Serafimovski T. Structural metallogenic features of the Lece – Chalkidiki zone: types of mineral deposits and distribution, Faculty of Mining and Geology – Shtip, Macedonia, **2**, 1993, 328 pp.
[14] Volcevska B., H. J. Voigt. Geological Heritage, World Heritage Studies, 2011, 15 pp.

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